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ARTICLE TYPE

# Low Temperature Solventless Synthesis and Characterization of Ni and Fe Magnetic Nanoparticles

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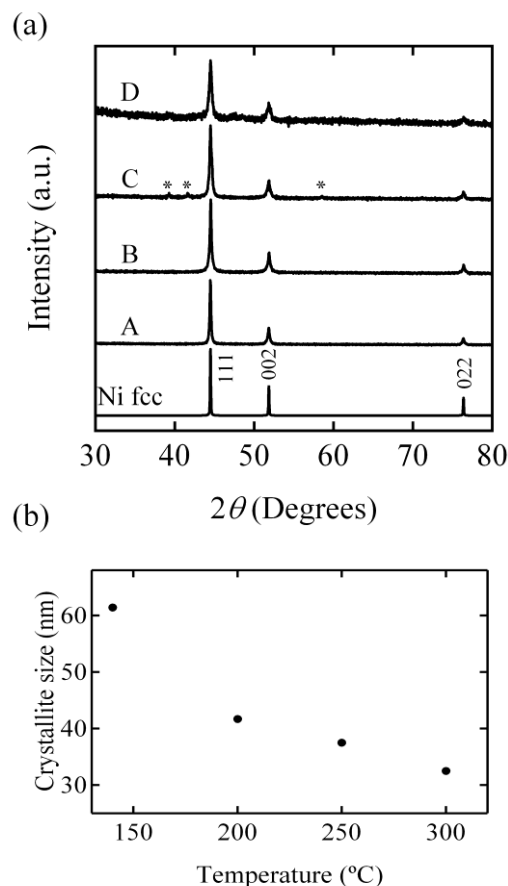
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We have successfully implemented a facile, one-pot solventless synthesis procedure starting from acetylacetonate salts and  $\text{CaH}_2$  to obtain carbon-coated ferromagnetic metallic Ni and Fe nanoparticles at low temperature. The use of  $\text{CaH}_2$  as a reductant drastically reduces reaction temperature down to 140 °C.

Metal nanoparticles (NPs) have been extensively studied in the past decades, mainly because of their unique magnetic, catalytic and optical properties.<sup>1</sup> All of these properties are strongly influenced by their size, shape and surface.<sup>2-5</sup> While ferromagnetic oxide particles have been quite common, metal NPs with ferromagnetism tend to have a higher saturation magnetization ( $M_s$ ) than their metal oxide counterparts.<sup>6</sup> However, unlike with oxides, in synthesizing and handling metal NPs, a challenging issue is how to avoid their oxidation. During the past decade, several materials have been developed as protective layers applicable for NPs such as polymers, silica and carbon.<sup>7-9</sup> Among them, carbon-based materials have many advantages as a coating material over polymers and silica, because of higher chemical and thermal stability as well as biocompatibility.<sup>6</sup>

Solventless synthesis, which requires only heating a precursory metal salt with an organic ligand, is one of the easiest methods to synthesize nanomaterials.<sup>7,9-12</sup> Chul *et al.* synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles from iron(II)-oleate complex<sup>7</sup>, while Jose *et al.* synthesized palladium NPs by heating palladium(II)-thiolate powder in air at 430 °C.<sup>10</sup> Cha *et al.* obtained silver NPs by heating silver(I)-oleate in a sealed pyrex tube (under 300 mTorr) at 290 °C.<sup>11</sup> Nakamoto *et al.* demonstrated thermolysis of ammonium gold(I) thiolate at 180 °C, to obtain gold NPs.<sup>12</sup>

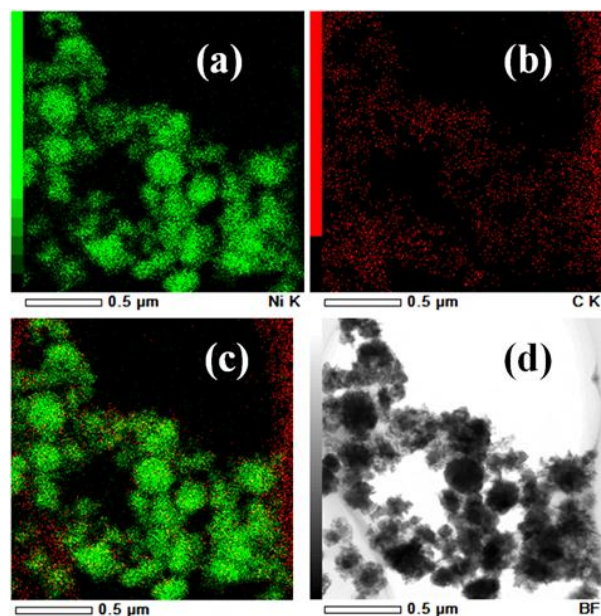
Solventless synthesis performed at low temperatures (typically less than 300 °C), is particularly attractive since it can produce monodispersed NPs.<sup>10-12</sup> At such low temperatures, the decomposition of organic ligands during reaction is greatly suppressed. Thus, the surface of the NPs is protected by the organic ligands, which effectively prevents coagulation and particle growth. Another merit of these low-temperature reactions is the suppression of the particle growth since the growth of NPs proceeds mainly by atoms added to the particle surface, leading to a monodispersed size distribution.<sup>7</sup> However, until now the low temperature (< 300 °C) solventless synthesis of metal NPs from a metal organic salt has been limited to easily reducible elements such as palladium, silver and gold.<sup>10-12</sup> There have been no reports about solventless synthesis



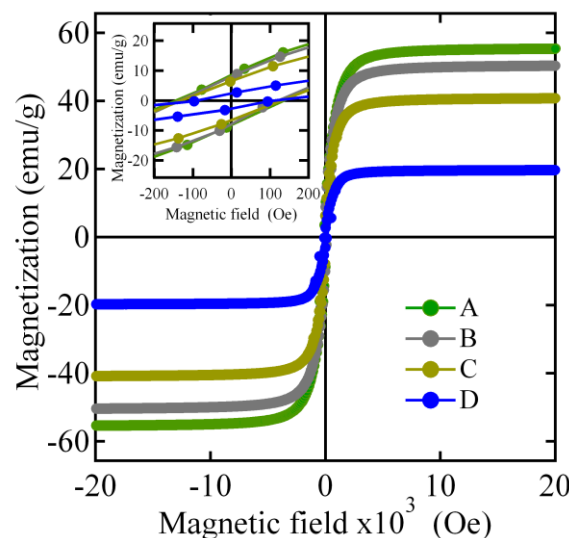
**Fig 1.** Powder XRD patterns; A, B, C and D represent the samples pre-pared with heat-treatment for 6 hours at 140 °C, 200 °C, 250 °C and 300 °C, respectively. Reference XRD pattern of bulk Ni with fcc lattice structure is also shown for comparison (bottom).<sup>15</sup> Asterisk (\*) represents hcp lattice structure peaks position (see Fig S3 in ESI).<sup>16</sup> (b) Crystallite size dependence on reaction temperature

of 3d transition metal NPs from a metal organic salt, since they are hardly reduced at low temperatures.<sup>10</sup>

Hereby, we report for the first time solventless synthesis method at low temperatures using  $\text{CaH}_2$  to obtain metallic Ni and Fe NPs directly from a metal organic salt. Several reports in solid state chemistry have shown that  $\text{CaH}_2$  is a very strong reductant for metal oxides at low temperatures (<300 °C).<sup>13</sup> We consider that reduction



**Fig 2.** (a) Ni mapping, (b) C mapping, and (c) Elemental mapping overlay of the sample, where Ni NPs core (green) are surrounded with carbon shell (red) and (d) TEM image of the same position



**Fig 3.** Plots of magnetization against applied field measured at 300 K for the samples heat-treated at different temperatures. Inset shows magnified view of the plot

temperatures for nanoparticle growth should be drastically lowered by the use of  $\text{CaH}_2$  as a reductant. Our recent work demonstrated that  $\text{CaH}_2$  reduces silica-coated iron oxide nanoparticles as low as at 180 °C.<sup>14</sup> This extraordinary strong reducing ability of  $\text{CaH}_2$  now enables us to develop a simple one-step synthesis of 3d transition metal NPs at low temperatures, where formation of metal NPs takes place directly from a metal organic salt. The ferromagnetic metals Ni and Fe are also known as pyrolysis catalysts for hydrocarbons into carbon and hydrogen. We find that with these carbon-rich metal salts, the nascent particles catalyze the decomposition of the ligand to form a carbon shell around the particle. This also probably avoids the formation of large particles, and also increases the particles' stability in air, especially important for elements such as Fe.

Fig. 1 shows powder X-ray diffraction (XRD) patterns of the products after heat-treatment at 140 °C, 200 °C, 250 °C and 300 °C for 6 hours, together with that of the bulk nickel.<sup>15,16</sup> Reduction can proceed only with  $\text{CaH}_2$  even at 300 °C (see Fig. S1 and Fig. S2 in ESI). There are three peaks in this range that could be assigned to {111}, {002} and {022} planes of face-centered cubic (fcc) structure of nickel.<sup>15</sup> Estimated lattice parameters are close to those of the bulk nickel (see Fig. S3 and Table S1 in ESI). As shown in Fig. 1(b), crystallite size becomes smaller with increasing reaction temperature. This rather unexpected dependency on reaction temperature, *i.e.*, decreasing particle size with increasing reaction temperature, might be explained by more nucleation sites at higher temperatures (see also Fig. S4 in ESI for details)

Metallic Ni NPs have been used as a catalyst to produce hydrogen (and carbon) from hydrocarbons. C/H elemental analysis suggests the formation of elemental carbon at higher reaction temperatures (See Table S2 in ESI). With increasing reaction temperature, carbon mass percentage increases. Carbon preferentially stays on the surface of the Ni nanoparticles, as shown with the transmission electron microscopy(TEM) image of Fig. 2.

We carried out magnetic measurements using magnetic fields up to 40,000 Oe at 300 K for the samples treated at various temperatures. The hysteresis curves of the samples are shown in Fig. 3. The sample synthesized at 140 °C has an  $M_s$  value close to that of the bulk nickel (55 emu/g).<sup>17</sup> We observed that both  $M_s$  and  $H_c$  are decreasing with increasing reaction temperature (see also Table S1 in ESI). This tendency can be understood due to the smaller grain size, and is consistent with the previous results, where  $M_s$  increases with increasing particles size (12 nm - 19 nm).<sup>18</sup> It is noted that presence of nickel's hexagonal close packed (hcp) phase should provide a negligible effect on  $M_s$  considering its small abundance shown by very low peak intensity in the XRD profile shown in Fig. 1. The decreasing behaviour of  $M_s$  could also be explained by particles synthesized at higher temperatures contained increased mass percentage of carbon (see Table S2 in ESI). From the low values of  $H_c$  we are able to say that the obtained metallic Ni NPs have soft magnetic properties.

In conclusion, we have successfully developed a simple solventless single step synthesis using metal organic salt and  $\text{CaH}_2$  to obtain ferromagnetic metallic nanoparticles at low temperatures. The use of  $\text{CaH}_2$  enabled drastic reduction of reaction temperature down to 140 °C in the case of nickel(II) acetylacetonate whereas reduction without  $\text{CaH}_2$  did not proceed even at 300 °C. Such low temperature reaction enables us to prevent decomposition of organic ligands during the reduction reaction, which acts as a source of amorphous carbon to give carbon-coated NPs. The size of the NPs could be controlled by changing the reduction temperature. This method can be further extended to other transition metal elements; carbon-coated metallic Fe NPs can be obtained by using iron(III) acetylacetonate (see Fig. S5 and Fig. S6 in ESI). Such carbon-coated ferromagnetic metallic nanoparticles have a wide range of applications from magnetic sensors to biomedical devices.

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## Notes and references

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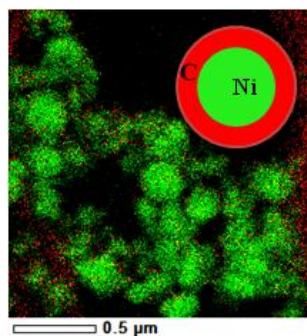
<sup>§</sup> CREST, Japan Science and Technology Agency (JST)

<sup>†</sup> Electronic Supplementary Information (ESI) available: Details of the synthesis and characterization methods, and complementary data (Figs. S1-S7 and Tables S1-S2). See DOI: 10.1039/b000000x

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## Graphical and Textual Abstract for the Table of Content



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A facile, one-pot solventless synthesis using  $\text{CaH}_2$  to obtain carbon-coated ferromagnetic metallic Ni/ Fe nanoparticles as low as 140 °C.